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COMPOSITION OF MATTER AND PROCESS FOR PREVENTING WATER-IN-OIL TYPE EMULSIONS RESULTING FROM ACIDIZATION OF CALCAREOUS OIL-BEARING STRATA

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31 Claims. (Cl. 252—8.55)

This application is a division of my pending application for patent Serial No. 360,801, filed October 11, 1940, which subsequently matured as U. S. Patent No. 2,262,738, dated November 11, 1941.

This invention relates to the art or procedure commonly referred to as acidization of oil-bearing, calcareous strata or the like, and which consists in introducing a strong mineral acid into an oil well for the purpose of causing the acid to disintegrate, dissolve, or react with the calcareous, oil-bearing structure of the well, in a manner that results in an increase in the amount of crude petroleum obtained from the oil-bearing strata.

Many oil wells, after being subjected to acidization, produce emulsions, frequently of a very refractory nature, that have to be demulsified or subjected to chemical, electrical, or similar treatments, in order to recover the oil or valuable constituent of the emulsion. My invention has for its main object to prevent the formation of objectionable water-in-oil type emulsions resulting from acidization of oil wells; or stated in another way, one object of my invention is to provide a process or procedure by which the oil-bearing, calcareous structure of a well can be acidized to increase the oil production, without danger of the procedure causing the well to produce a product, which, after being discharged from the well, has to be treated with a demulsifying agent, or subjected to other treatment of the kind commonly employed for converting refractory petroleum emulsions into oil that can be sold to pipe lines and refineries. Such refractory emulsions which often follow conventional acidization, represent a transitory, rather than a permanent situation; but even if lasting only for a few weeks, they are extremely objectionable.

Another object of my invention is to provide a new composition of matter that is particularly adapted for use in the operation of acidizing the calcareous structure in a way to increase the amount of crude petroleum obtainable from said structure, without, however, converting said crude petroleum into an objectionable emulsion.

My new process, briefly stated, consists in causing an emulsion-preventing agent of the kind hereinafter described, to be mixed with, dissolved in, or commingled with the fluids, liquids, or liquid mixture in an oil well that has been subjected to or which is being subjected to acidization, prior to emergence of said fluids, liquids, or liquid mixtures from the well. Said emulsion-preventing agent consists of a chemical compound or condensation product derived from the following reactants; an alkylolamine free from any amino-nitrogen atom not linked to a hydroxy-hydrocarbon radical; a higher molecular weight carboxylic acid; and a hydroxylated polyamine containing at least one amino nitrogen atom not directly linked to a hydroxy hydrocarbon radical, and preferably, at least two such nitrogen atoms free from direct linkage with a hydroxy hydrocarbon radical.

The mixture of such reactants is in the proportion that there is at least one mole of each type of amino compound for each mole of high molecular weight carboxy acid. The condensation process consists essentially in heating the mixture at a temperature of about 100° C., or higher, but below the temperature of decomposition of the resulting hydrotropic material, and conducted so as to effect a condensation between the three reactants. The maximum temperature generally employable is approximately 300° C. The preferred range is about 235–300° C.; and in a general way, 250–275° C. represents an optimum range for a variety of the reactants employed.

The composition of the condensation products obtained in the manner briefly outlined above is unknown. For this reason many of the properties of the materials are unpredictable. It is surprising to find that such materials are stable for an extended period of time in half-concentrated hydrochloric acid or other similar mineral acids. It is likewise remarkable to note that such solutions in acid, and particularly in relatively low ratios, as hereinafter described, give a very pronounced lowering of the surface tension. This is especially true in such compounds or condensation products that are derived at relatively high temperatures, and especially if derived from polyamino reactants of the kind having at least two amino nitrogen atoms not directly linked to a hydroxy hydrocarbon radical. This is all the more remarkable, in view of the relatively weak stability of esters and amides toward strong acids. It is difficult to indicate a probable structure for

such compounds which would account for their resistance to decomposition in strong acid solution.

In practising my process the emulsion-preventing agent is caused to act upon or come in contact with the fluids, liquids, or liquid mixture in a well that has been subjected to acidization, either while said fluids or liquids are at the bottom of the well, or while said fluids or liquids are traveling upwardly to the surface of the ground, but the particular procedure, the means used to effect the mixing or commingling of said emulsion-preventing agent with the well fluids or liquids, and the particular time when said mixing is effected, are immaterial, so long as said emulsion-preventing agent becomes mixed with, dissolved in, or commingled with the cognate fluids of the well or the liquids or liquid mixture resulting from the acidization operation (the oil and the reaction product of the mineral acid on the calcareous structure), prior to emergence from the well. Equally good results may be obtained by the following procedure, to wit:

(a) Introducing the emulsion-preventing agent, preferably in aqueous solution, prior to the introduction of the mineral acid into the well;

(b) Introducing the emulsion-preventing agent along with the mineral acid, i. e., dissolved in said acid; and

(c) Introducing the emulsion-preventing agent, preferably in aqueous solution, immediately after the introduction of the mineral acid.

The composition of matter that I have devised for acidizing the calcareous oil-bearing structure of oil wells, consists of the emulsion-preventing agent above described, mixed with, dissolved in, or combined with a strong mineral acid, such as hydrochloric acid, nitric acid, sulfuric acid, sulfamic acid, or mixtures of the same. My preference is to use hydrochloric acid whose concentration is at least equal to approximately half strength commercial 18 Bé. acid, as I have found that when such an acid is mixed with approximately 0.01% to 2.5% of the herein contemplated emulsion-preventing agent or agents, one obtains a new composition of matter that is perfectly stable and homogeneous, and which exhibits unusual properties, particularly when said acid mixture or new composition of matter is employed in the acidization of oil-bearing strata. However, I wish it to be understood that my invention, i. e., the process and composition of matter herein described, is not restricted to the use of hydrochloric acid, but instead, contemplates the use of any suitable strong mineral acid, several of which have previously been described as being usable in place of hydrochloric acid. Similarly, I wish it to be understood that the new composition of matter herein described may have other or additional uses, such, for example, as in the acidization of oil-bearing strata which do not produce emulsions. The hydrochloric acid or the like that is employed, may or may not have present other addition agents intended to make the acid particularly adapted to most localized conditions, which sometimes arise in the course of acidization. It should be emphasized that what is said hereinafter as to the utility and effectiveness of the composition of matter herein contemplated, applies with equal force and effect to the process which forms part of the present invention.

A number of problems have been involved in the introduction of strong mineral acid into oil-bearing strata of the kind containing calcium carbonate, magnesium carbonate, mixtures of same, with siliceous material, or material which is dolomitic in character, and commonly referred to as calcareous structures. One problem is the prevention of corrosion, or damage to the metallic working parts of the well into which the acid is introduced. This has been overcome in various ways, such as by the use of an inhibitor. For the sake of brevity, reference is made to the following patents which give a cross-sectional view of the art related to acidization, although there are in addition certain other practical elements which are well known: U. S. Patent No. 1,877,504, dated Sept. 13, 1932, Grebe & Sanford; 1,891,667, Dec. 20, 1932, Carr; 1,911,446, May 20, 1933, Grebe & Sanford; 1,990,969, Feb. 12, 1935, Wilson; 2,011,579, Aug. 20, 1935, Heath & Fry; 2,024,718, Dec. 17, 1935, Chamberlain; 2,038,956, Apr. 28, 1936, Parkhurst; 2,053,285, Sept. 8, 1936, Grebe; 2,128,160, Aug. 23, 1938, Morgan; 2,128,161, Aug. 23, 1938, Morgan; and 2,161,085, June 6, 1939, Phalen.

As has been previously stated in the acidization of oil-bearing, calcareous strata or the like, it has been found necessary, in some instances to add certain other materials or compounds which give additional desirable effects, at least under certain conditions. For instance, hydrofluoric acid or fluorides, have been added to intensify the action of the hydrochloric acid used to treat the well. Possibly this is related to the action on siliceous matter in the calcareous structure. The reason for the addition of inhibitors has been previously indicated. Sometimes it has been desirable to add tenacious foam-producing agents, such as glue, gelatin, or the like. In other instances, it has been desirable to add calcium sequestering compounds, such as sodium hexametaphosphate. In other instances reducing agents have been added to keep any dissolved iron salts in the ferrous state. Isopropyl alcohol or the like is sometimes added as a surface tension depressant. Thus, the addition of various other auxiliary agents, commonly referred to as addition agents, is well known.

I have found that the materials or products which I contemplate adding to the hydrochloric acid or the like to produce my new composition of matter, or to act as an emulsion-preventing agent in my new process, do not interfere in any manner with the functional effect of other conventional acidizing addition agents. Of course, any single example may contain no additional agent at all; it may contain one or more, depending upon the particular local conditions and use. As far as I am aware, the herein-contemplated compounds which are added to hydrochloric acid, or any other suitable mineral acid, such as a mixture of hydrochloric acid and hydrofluoric acid, do not replace other addition agents which have been added for various other purposes. For the sake of brevity, reference will be made to hydrochloric acid as illustrating any suitable mineral acid. It is understood, of course, that such hydrochloric acid may or may or may not contain various amounts of hydrofluoric acid.

As previously indicated, the emulsion-preventing agents herein described have the effect of preventing emulsions, when an oil well is turned into production after the acidizing operation Many oil wells are acidized without subsequently producing any emulsions; or the emulsions, i

produced, are self-resolving, or readily susceptible to any moderate breaking action. However, certain wells, particularly those located in western Kansas and certain wells in Illinois, when acidized by conventional processes, yield particularly refractory emulsions. This is a rather surprising situation, insofar that the spent acid results in a solution having approximately 20% of calcium chloride present, and having a pH value of approximately 3.5 to 5. One would expect the increased acidity over that of most natural brines to decrease the stability of the emulsion. One would also expect that the increased electrolyte content of the dispersed phase would decrease the stability of the emulsion. The increased specific gravity differential should have a similar de-stabilizing effect. Actually, in a number of instances, this is not the case, and such emulsions have resulted in unusual problems. In its broadest aspect, then, the agents herein contemplated may be used simply as emulsion-preventers, in connection with the acidization of subterranean strata.

The most concentrated hydrochloric acid, ordinarily available, is about 36% HCl strength. The commercial acid of this strength or somewhat weaker, is usually diluted with an equal quantity of water before it is used for acidization; i. e., the acid used in acidization may vary from 14% to 16.5% HCl, although acid varying in strength from 5% to 20% HCl has been employed. It is entirely feasible to add an agent to the acid as produced at the point of manufacture, thus exemplifying the composition of matter feature of the present invention. For instance, if desired, 0.02% to 5% of the contemplated agent may be added to the concentrated hydrochloric acid in manufacture. Such acid can be diluted to a suitable point before being employed in the acidization process. Thus, such concentrated acid can be diluted, for instance, half and half, so that the reagent is present in the dilute product within the ratio suggested previously, to wit: 0.01% and 2.5%. In many instances, the use of between 0.05% and 0.5% represents an acceptable average range.

In actual practice the hydrochloric acid obtained by a person or firm responsible for acidizing operations, may be used, in some instances, on oil-bearing strata, which do not form severe or refractory emulsions, and thus no advantage is obtained by adding a composition of the kind herein contemplated in comparison with ordinary acid. Then too, some calcareous, oil-bearing strata which produces severe emulsions, may require more or less of the agent of the kind herein contemplated than would be necessary in some other strata. For this reason, in the practical aspect it is generally desirable to add the agent of the kind herein contemplated to the dilute acid, so as to be suitable for the specific local conditions which require treatment. The suitable range of ratios for ordinary half-strength has been indicated.

As has been previously suggested, one may also add to the acid intended for acidization, various other reagents or addition products of the kind described in the aforementioned list of patents, without affecting the operation of the emulsion-preventing agent that I employ, and without danger of said emulsion-preventing agent interfering with the effectiveness of such other acidization addition products. Likewise, it has been indicated that one need not necessarily employ my emulsion-preventing agent in the form of an addition agent, which is added to or mixed with the acid used in the acidizing step. Instead, my emulsion-preventing agent may be introduced in suitable aqueous solution, preferably in fairly concentrated solution, for instance, 1–5%, prior to the acidizing step, or immediately after the acidizing step. The method of introduction is, of course, any conventional method, and preferably, employs the same apparatus and procedure used for introducing the acid. For convenience, however, and in the most preferred form, my invention is exemplified by employing as an integral part thereof the composition of matter herein contemplated, to wit, hydrochloric acid or the like, containing in stable admixture, agents of the kind subsequently to be described and within the percentage range indicated.

The ineffectiveness of most ordinary demulsifiers for preventing the formation of water-in-oil type emulsions, resulting from acidization, is readily understandable. Ordinary demulsifiers either are not soluble in half-strength hydrochloric acid, or its equivalent, or they are not soluble in spent brine of the kind previously mentioned, i. e., brine containing roughly the equivalent of 20% of calcium chloride, and having a pH of 3.5 to 5. Furthermore, if soluble at all, they are generally decomposed; and if they do not decompose under ordinary conditions, they at least decompose under the conditions which involve the necessary pressure employed in acidization. Then too, in some instances where such demulsifiers appear to meet all other requirements, they apparently precipitate out on the face of the pay sand or oil-bearing strata, and may even reduce instead of increase the oil production, as compared with results obtained by ordinary acid. There are a number of other reasons not necessary to explain, which prevent ordinary demulsifiers from being effective. It is possible that the characteristic properties of the new composition of matter herein described, make it adaptable for use in other arts with which I am not acquainted; but it may be apparent to others. It is also possible that the stable mixture of the kind described, i. e., certain agents dissolved in strong mineral acid, have other properties which I have not investigated, and in view of such properties, such mixture is particularly adaptable for the particular use herein described.

As has been stated, condensation materials of the kind previously described are obtained from higher molecular weight carboxy acids, and particularly monocarboxy acids or their functional equivalents, such as the acyl halide, ester, amide, etc. The expression "higher molecular weight carboxy acids" is an expression frequently employed to refer to certain organic acids, particularly monocarboxy acids, having more than 6 carbon atoms and generally less than 40 carbon atoms. The commonest examples include the detergent-forming acids, i. e., those acids which combine with alkalies to produce soap or soap-like bodies. The detergent-forming acids, in turn, include naturally-occurring fatty acids, such as abietic acid, naturally-occurring petroleum acids, such as naphthenic acids, and carboxy acids produced by the oxidation of petroleum. As will be subsequently indicated, there are other acids which have somewhat similar characteristics and are derived from somewhat different sources, and are different in structure, but can be included in the broad generic term previously indicated.

Among sources of such acids may be mentioned traight chain and branched chain, saturated nd unsaturated, carboxylic, aliphatic, alicyclic, atty, aromatic, hydroaromatic and aralkyl acids, ncluding caprylic acid, butyric acid, heptylic acid, aproic acid, capric acid, pimelic acid, sebacic cid, erucic acid, saturated and unsaturated ligher molecular weight aliphatic acids, such as he higher fatty acids containing at least 8 car- on atoms, and including, in addition to those nentioned, melissic acid, stearic acid, oleic acid, icinoleic acid, diricinoleic acid, triricinoleic acid, olyricinoleic acid, ricinostearolic acid, ricinoleyl actic acid acetylricinoleic acid, chloracetylricin- oleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, undecylenic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, cocoanut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soyabean oil, peanut oil, castor oil, seal oils, whale oil, shark oil, and other fish oils, teaseed oil, partially or completely hydrogenated animal and vegetable oils, such as those mentioned; hydroxy and alpha-hydroxy higher carboxylic aliphatic and fatty acids, such as dihydroxystearic acid, dihydroxy palmitic acid, dihydroxybehenic acid, alphahydroxy capric acid, alphahydroxy lauric acid, alphahydroxy myristic acid, alphahydroxy cocoanut oil mixed fatty acids, alphahydroxy margaric acid, alphahydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes, such as beeswax, spermaceti, montan wax, Japan wax, coccerin, and carnauba wax. Such acids include carnaubic acid, cerotic acid, lacceric acid, montanic acid, psyllastearic acid, etc. As suggested, one may also employ higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons; resinic and hydroabietic acid; aralkyl and aromatic acids, such as benzoic acid, Twitchell fatty acids, naphthoic acid, carboxydiphenyl pyridine carboxylic acid, hydroxybenzoic acid, and the like. Other suitable acids include phenylstearic acid, benzoylnonylic acid, cetyloxyacetic acid, chlorstearic acid, fencholic acid, cetyloxybutyric acid, etc. Alkylolamines, in which the amino nitrogen atoms are linked to a hydroxyhydrocarbon radical, are exemplified by the commoner alkylolamines, such as monoethanolamine, diethanolamine, triethanolamine, dialkylolamines, diethyl ethanolamine, monoethyl alkylolamine, monopropanolamine, dipropanolamine, tripropanolamine, butanolamine, pentanolamines, hexanolamines, cyclohexanolamine, cyclohexyl ethanolamine, benzyl ethanolamine, N-phenyl ethanolamine, laurylolamine, and also the alkylolamines of glycerine, sugar, and other mono- and polyvalent alcohols and aryl and cyclo alkylolamines. The polyamino type of amines, such as tetraethanol ethylenediamine, tetrapropanol ethylenediamine, or the like, may be employed.

I prefer to use amines free from an aryl radical, and more particularly, prefer to use common alkylolamines in which the alkylene radical contains two or three carbon atoms. More particularly, I prefer to use triethanolamine, because of its commercial availability, and also because I have found that the tertiary amines appear to give the best results. Secondary amines, for instance, diethanolamine, appear to give better results than primary amines, such as monoethanolamine.

The hydroxylated polyamines, characterized by the presence of at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, are well known compounds. They may be obtained in various ways. The commonest procedure is to treat a polyamine with an alkylene oxide, or its equivalent, such as ethylene oxide, propylene oxide, glycidol, or the like. The commoner polyamines which can be so treated with an oxy-alkylating agent include the following: ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; pentaethylene hexamine; propylene diamine; dipropylene triamine; tripropylene tetramine; tetrapropylene pentamine; pentapropylene hexamine, etc. In some instances such amines may be treated with an alkylating agent or the like, so as to introduce an alkyl, aralkyl, or alicyclic radical into the compound as a substitute for an amino hydrogen atom. For instance, one may obtain diethyl tetraethylene pentamine in the conventional manner using ethyl iodide or the like as a alkylating agent.

In any event, having selected a suitable polyamine, the product is then treated with any acceptable oxy-alkylating agent, such as ethylene oxide, propylene oxide, and the like. In view of the lower cost of ethylene oxide, and in view of its greater activity, it is most frequently employed. For instance, ethylene diamine can be treated with one mole of ethylene oxide to produce hydroxy ethylene diamine. Diethylene triamine can be treated with three moles of ethylene oxide so as to yield triethanol diethylene triamine. Triethylene tetramine can be treated with four moles of ethylene oxide to yield tetraethanol triethylene tetramine. Similarly, one can obtain tetraethanol tetraethylene pentamine, or tetraethanol pentaethylene hexamine. One can employ propylene oxide or glycidol to give similar products. In view of the fact that the most inexpensive polyamine now available is tetraethylene pentamine, I prefer to treat tetraethylene pentamine with three moles of ethylene oxide, four moles of ethylene oxide, or five moles of ethylene oxide, to give the corresponding triethanol, tetraethanol, and pentaethanol derivatives, and to employ such derivatives.

The condensation products employed are manufactured by a simple heat condensation process. The mixture of the three classes of reactants is subjected to a temperature sufficient to produce the desired condensation. As has previously been pointed out, one need not use the high molal carboxy acids themselves, but any suitable source of the desired acyl radical may be employed. I have found that particularly effective condensation products are obtained if one employs an unsaturated fatty acid or a compound thereof along with triethanolamine and one of the hydroxylated polyamine type compounds. It is preferable that these condensation products be free from aryl radicals, and that they should be obtained at the higher temperature indicated, i. e., about 235–275° C. It is most advantageous to prepare this type of condensation product from the naturally-occurring glycerides; or, if prepared from the fatty acid, it is desirable to add at least one mole of glycerol to the mixture for each three moles of fatty acid employed.

It will be pointed out hereafter that the con-

densation products themselves may be utilized for other purposes than in connection with the acidization of oil-bearing strata. In order to obtain light colored condensation products, it is most desirable to use glass-lined apparatus or vessels prepared from suitable non-ferrous alloys. It is most desirable that the reactants be stirred slowly during the polymerization process, and it is usually advantageous to make some arrangement for an elimination of water which may be formed. In the simplest aspect, this is most readily accepted by employment of a hot condenser in connection with the reaction vessel. The temperature of such hot condenser is preferably slightly above 100° C., so as to permit the escape of water vapor, but to prevent the loss of any of the reactants by volatilization. In some instances it may be necessary to conduct the reaction for a fairly long period of time, for instance, 8–20 hours, or thereabouts. In many cases it is desirable to react the finished condensation product with suitable acid, such as lactic acid, acetic acid, or the like, particularly when the condensation product is employed for some purpose other than acidization of calcareous structure.

In order to illustrate the manufacture of such condensation products, attention is directed to the following examples, in which the expression "pound mole" is used to indicate the molecular weight in pounds:

Example 1

A mixture is prepared using one pound mole each of the following: teaseed-oil fatty acid, triethanolamine and tetraethanol tetraethylene pentamine. Such mixture is for 3–6 hours at 235–275° C.

Example 2

Pentaethanol tetraethylene pentamine is substituted for tetraethanol tetraethylene pentamine, in Example 1.

Example 3

Triethanol tetraethylene pentamine is substituted for tetraethanol tetraethylene pentamine in Example 1.

Example 4

Tetrapropanol tetraethylene pentamine is substituted for tetraethanol tetraethylene pentamine in Example 1.

Example 5

Pentapropanol tetraethylene pentamine is substituted for tetraethanol tetraethylene pentamine in Example 1.

Example 6

Tripropanoltetraethylene pentamine is substituted for tetraethanol tetraethylene pentamine in Example 1.

Example 7

Triisopropanol triisopropanolamine is substituted for triethanolamine in Examples 1 through 6.

Example 8

Diethanolamine is substituted for triethanolamine in Examples 1 through 6.

Example 9

Tris(hydroxymethyl)aminomethane is substituted for triethanolamine in Examples 1 through 6.

Example 10

Glycerolamine is substituted for triethanolamine in Examples 1 through 6.

Example 11

Tetraethanol ethylenediamine is substituted for triethanolamine in Examples 1 through 6.

Example 12

Tetraethanol propylenediamine is substituted for triethanolamine in Examples 1 through 6.

Example 13

Tetraethanol butylene diamine is substituted for triethanolamine in Examples 1 through 6.

Example 14

Tetraethanolamylene diamine is substituted for triethanolamine in Examples 1–6, inclusive.

Example 15

Other unsaturated fatty acids, such as ricinoleic acid, soyabean fatty acids, corn oil fatty acids, and the like are substituted for teaseed oil acids in Examples 1–14, inclusive.

Example 16

A saturated fatty acid, or mixture thereof, such as cocoanut oil fatty acids is used in place of teaseed oil fatty acid in Examples 1–14, inclusive.

Example 17

Naphthenic acids are employed in place of teaseed oil fatty acids in Examples 1–14, inclusive.

Example 18

The glycerides are used in place of the fatty acids in Examples 1–16, inclusive, employing a pound mole of glycerides in place of 3 pound moles of fatty acids.

Example 19

The fatty acids are employed as in Examples 1–16, inclusive, but glycerol is added to the mixture prior to heating. 1 mole of glycerol is used for each 3 moles of fatty acid.

Example 20

The amount of glycerol in the prior example is doubled.

Example 21

Diglycerol is substituted for glycerol in Examples 19 and 20.

Example 22

In preceding examples the molecular proportions of hydroxylated amine of the triethanolamine type is doubled.

Example 23

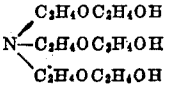
In Examples 1–22, inclusive, the molar proportions of hydroxylated amine of the triethanolamine type is tripled.

Example 24

Examples 1–23, inclusive, are repeated, using temperatures approximating the maximum mentioned, i. e., 300° C.

Example 25

Examples, 1–24, inclusive, are repeated, substituting polyethanolamine, such as



for triethanolamine in the previous examples. Similarly, one may employ products obtained by the action of glycidol or triethanolamine instead of ethylene oxide. If desired, the same sort of product may be obtained by converting triethanolamine into the monoalkylate, i. e., by replacing one hydroxyl hydrogen atom by a sodium atom, and then reacting such compound, mole for mole, with glycerol monochlorhydrin, so as to eliminate sodium chloride. A product of this type is particularly suitable as a substitute for triethanolamine in the previous example.

Another procedure of distinct value is to follow Example 20, but instead of doubling the amount of glycerol, to triple or quadruple the same. Instead of glycerol, one may use any polyhydric alcohol which is not decomposed by the heat of condensation, such as ethylene glycol, diethylene glycol, propylene glycol, or the like.

It is to be emphasized that one may use any suitable detergent-forming acid, including rosin acids; and for that matter, one may employ a high molal carboxy acid which is not of the detergent-forming type. One may employ arylamines and hydroxylated arylamines.

Wherever the term "condensation product" is employed, it will be understood to cover a reaction product between the high molar carboxy acid or its equivalent, the alkylolamine of the triethanolamine type, and the hydroxylated polyamine, wherein water or acid or the like is split out as a result of the union of the molecules of the three types of reactants. Similarly, the expression "condensing" is employed to refer specifically to the process whereby such condensation takes place.

All the chemical compounds previously described are water-soluble as such, or when dissolved in dilute acid or acid of the concentration indicated. Such compounds may be combined not only with mineral acids, but also with organic acids, such as acetic acid, lactic, stearic acid, or the like. For this reason they can be used without difficulty in aqueous solution as an emulsion-prevention agent by injecting such aqueous solution into the oil-bearing strata prior to acidization, or immediately after acidization. Such injection is made by conventional means, as, for example, the same apparatus or mechanical device employed for injecting acid into the well or oil-bearing strata. Furthermore, substantially all the compounds above described are soluble in hydrochloric acid of a strength corresponding to approximately 15%. Furthermore, substantially all the compounds of the type indicated are soluble in concentrated hydrochloric acid. Commercial hydrochloric acid is ordinarily available in grades from approximately 18° Bé., corresponding to approximately 28% anhydrous acid, to 22 Bé. corresponding to approximately 35.2% anhydrous acid. Some commercial hydrochloric acid is available in a strength which approximates the C. P. grade or slightly less than 37% anhydrous acid.

Needless to say, my new composition of matter can be prepared readily in any convenient form. The expression "new composition of matter," in this present instance, is intended to refer to the combination or mixture obtained by combining a condensation product of the kind described with hydrochloric acid or the like, as has been described.

The selected compound may be dissolved in concentrated hydrochloric acid without dilution. The percentages employed have already been indicated. Such a concentrated hydrochloric acid may or may not contain some hydrofluoric acid. Likewise, if desired, the emulsion-preventing agent may be dissolved in water, and such aqueous solution added to the hydrochloric acid or the like, in order to dilute the same to the desired concentration. Another procedure, of course, is to add the particular chemical compound which has been selected as the emulsion-preventing agent. The percentage of chemical compound of the kind herein described is added within the range of 0.01% to 5%.

In the hereto appended claims, reference to the use of the condensation product is intended to include the base form, i. e. the chemical combination with water, and also the salt form, such as the lactate, acetate, citrate, or the like.

It has been previously pointed out that in the present instance the expression "new composition of matter" is intended to refer to the combination of a condensation product of the kind described and hydrochloric acid or some other mineral acid. However, as far as I am aware, the condensation product or products herein described are per se new compositions of matter, and more specifically, are cation-active materials. There is a wide variety of uses for surface-active materials. See, for example, U. S. Patent No. 2,174,131, dated September 26, 1939, to Lubs. Some of these purposes are particularly adapted to the use of a cation-active material or a cation-active material which is at least self-emulsifiable. In such instances, a material of the kind herein contemplated, particularly the preferred type, is specifically suitable. Briefly, then, specific uses for my product per se include use as wetting, detergent, and leveling agents in the laundry, textile, and dyeing industry; as wetting agents and detergents in the acid washing of fruit and in the acid washing of building stone and brick; as a wetting agent and spreader in the application of asphalt in road building and the like; as a constituent of soldering flux preparations; as a flotation reagent in the flotation separation of various minerals; for flocculation and coagulation of various minerals; for flocculation and coagulation of various aqueous suspensions containing negatively charged particles such as sewage, coal washing waste water, and various trade wastes and the like; and as germicides, insecticides, and emulsifiers for cosmetics, spray oils, water-repellent textile finish, etc. These uses are by no means exhaustive.

I have found such condensation products per se to be excellent demulsifiers for water-in-oil emulsions, particularly the kind which occur in the production of crude oil and of the kind which occur in de-salting procedure, as employed in refineries. Such condensation products may also be used as break-inducers in doctor treatment of the kind intended to sweeten gasoline. See U. S. Patent No. 2,157,223, dated May 9, 1939, to Sutton.

Furthermore, such condensation products per se may be employed as intermediates for combination with other reactants so as to obtain added products of utility. For instance, such condensation products per se may be reacted with polybasic acids, such as phthalic acid maleic acid, oxalic acid, succinic acid, adipic acid, and the like, or their fractional salts, or fractional esters, such as sodium acid phthalate octyl acid phthalate, dodecyl acid phthalate triricinolein monophthalate, triricinolein di-

phthalate, and the like, to give new compounds or compositions of matter which have utility in various of the arts previously enumerated.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids, of a well prior to emergence, a condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyalkylene amine containing at least one nitrogen atom not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical.

2. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, a condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least one nitrogen atom not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical.

3. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, a condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical.

4. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, a condensation product obtained by reacting (A) a reactant containing an unsaturated fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) unsaturated fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical.

5. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, a condensation product obtained by reacting (A) a reactant containing a ricinoleyl radical and a glyceryl radical selected from the class consisting of (*a*) ricinoleins and (*b*) a mixture of a glycerol and ricinoleic acid; the proportion of the components of the said mixture being at least one-third mole of glycerol for each mole of ricinoleic acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acid radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical.

6. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of triricinolein, at least one mole of an alkylolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical.

7. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of triricinolein, at least one mole of an ethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical.

8. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of triricinolein, at least one mole of triethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical.

9. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emer-

gence, the condensation product derived from one mole of triricinolein, at least one mole of diethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical.

10. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of a higher molecular weight carboxy acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

11. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of a detergent-forming acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

12. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of a higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

13. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

14. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

15. A process for preventing water-in-oil emulsions resulting from the acidization of calcareous oil-bearing strata, which consists in introducing into the cognate fluids of a well prior to emergence, the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol.

16. A new composition of matter, comprising strong mineral acid and the condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole ofthe glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyalkylene amine containing at least one nitrogen atom not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said mineral acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

17. A composition of matter, comprising hydrochloric acid and the condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine and (C) a hydroxylated polyalkylene amine containing at least one nitrogen atom not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

18. A composition of matter, comprising hydrochloric acid and the condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least one nitrogen atom not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

19. A composition of matter, comprising hydrochloric acid and the condensation product obtained by reacting (A) a reactant containing a fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid

having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

20. A composition of matter, comprising hydrochloric acid and the condensation product obtained by reacting (A) a reactant containing an unsaturated fatty acid acyl radical and a glyceryl radical selected from the class consisting of (*a*) unsaturated fatty acid glycerides derived from fatty acids having at least 8 and not more than 32 carbon atoms and (*b*) a mixture of a glycerol and a fatty acid having at least 8 and not more than 32 carbon atoms; the proportions of the components of the said mixture being at least one-third mole of the glycerol for each mole of said fatty acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

21. A composition of matter, comprising hydrochloric acid and the condensation product obtained by reacting (A) a reactant containing a ricinoleyl radical and a glyceryl radical selected from the class consisting of (*a*) ricinoleins and (*b*) a mixture of a glycerol and ricinoleic acid; the proportion of the components of the said mixture being at least one-third mole of glycerol for each mole of ricinoleic acid, with (B) an alkylolamine, and (C) a hydroxylated polyethylene amine containing at least two nitrogen atoms not directly attached to a hydroxy hydrocarbon radical; the proportion of B to A being at least one mole of the alkylolamine for each fatty acyl radical and the proportion of C to A being at least one mole of amine for each fatty acid acyl radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

22. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of triricinolein, at least one mole of an alkylolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

23. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of triricinolein, at least one mole of an ethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

24. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of triricinolein, at least one mole of triethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

25. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of triricinolein, at least one mole of diethanolamine, and at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

26. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of a higher molecular weight carboxy acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

27. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of a detergent-forming acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

28. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of a higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

29. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyalkylene amine containing at least one amino nitrogen atom not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

30. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine,

at least one mole of a hydroxylated polyalkylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

31. A composition of matter, comprising hydrochloric acid and the condensation product derived from one mole of an unsaturated higher fatty acid, at least one mole of an alkylolamine, at least one mole of a hydroxylated polyethylene amine containing at least two amino nitrogen atoms not directly attached to a hydroxy hydrocarbon radical, and at least one-third mole of glycerol, said hydrochloric acid in uncombined form being present on a large molal excess basis in comparison with the condensation product.

MELVIN DE GROOTE.